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Published in:
Chemical Communications

DOI:
10.1039/c2cc35298b

Publication date:
2012

Electronic Suporting Information (ESI) for:

Production of large graphene sheets by exfoliation of graphite under high power ultrasound in the presence of tiopronin

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Chemicals. Tetrachloroauric acid ($HAuCl_4 \bullet 3H_2O$), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), ascorbic acid, concentrated HCl, cetyltrimethyl ammonium bromide (CTAB) and poly(vinylpyrrolidone) (PVP, Mr = 40,000) were purchased from Aldrich. All solvents were obtained from commercial suppliers and used without further purification. Milli-Q water with a resistivity 18.2 MΩ cm was used in gold nanorods synthesis. Graphite was purchased from Bay Carbon, Inc. (SP-1 graphite powder, www.baycarbon.com).

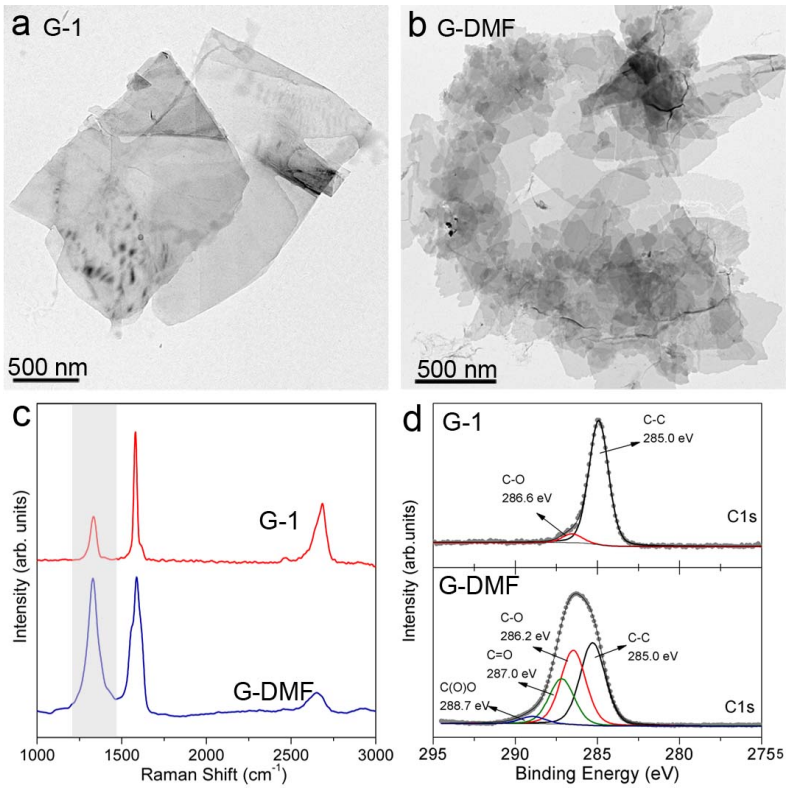
Gold Nanorods preparation, Au-NRs. A solution of gold seed was prepared by borohydride (30 mM, 0.3ml) reduction of $HAuCl_4$ (0.25 mM, 5 ml) in aqueous cetyl trimetylammonium bromide,

CTAB solution (0.1M). An aliquot of the seed solution (24 µl) was added to a growth solution (10 ml) containing CTAB (0.1M), $HAuCl_4$ (0.5 mM), ascorbic acid (0.8 mM), silver nitrate (0.12 mM), and HCl (18.6 mM). The mixture was left undisturbed for 4 hours at 27 ˚C.

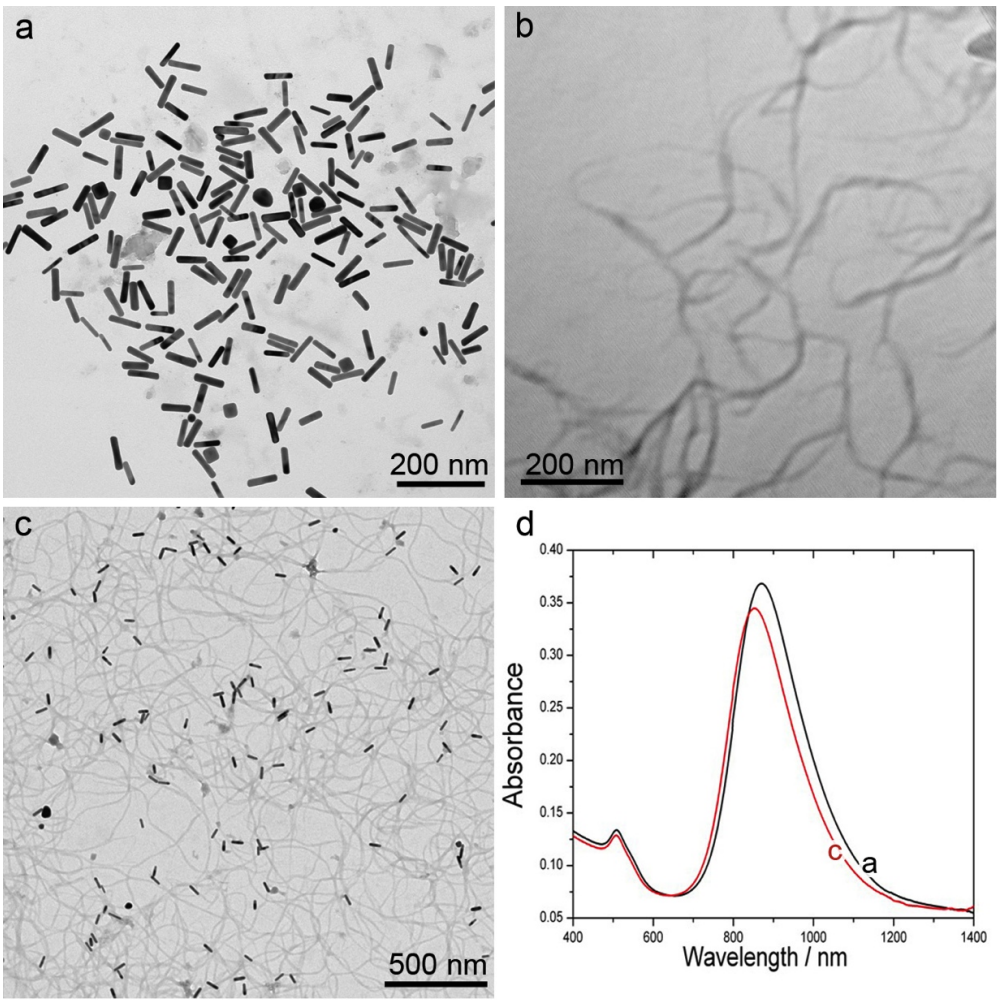
Surface functionalization of gold nanorods - PVP coating. Typically, a suspension of as-prepared gold nanorods (10 ml) was centrifuged at 8000 rpm for 15 min and the precipitate was redispersed in Milli-Q water (5 ml). Subsequently, 5 ml of CTAB-coated gold nanorods were mixed with an aqueous solution of PVP (1.2 mM, 5 ml) and stirred overnight. The mixture was centrifuged at 4500 rpm for 60 min and the precipitate was re-dispersed in 5 ml of DMF.

Characterization techniques. The optical characterization was carried out by UV-vis-NIR spectroscopy with a Cary 5000 spectrophotometer using 10 mm path length quartz cuvettes. TEM measurements were performed on a TEM Philips EM208, using an accelerating voltage of 100 kV. Samples were prepared by drop casting from the dispersion onto a TEM grid (200 mesh, Nickel, carbon only). An aberration corrected TEM (FEI TITAN 50-80) was used at 80kV in order to visualize the atomic structure of the graphene sheets. X-ray photoelectron spectroscopy (XPS) data were collected using an SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatic Al Kα X-ray source (hν=1486.6 eV); the photoelectron take off angle was 37° and the energy resolution was set to 1.2 eV. For points were analysed on each sample to check for homogeneity. An electron flood gun was used to compensate for sample charging; the base pressure during the measurement was $3x10^{-10}$ mbar. Binding energies were referenced to the Au $4f_{7/2}$ core level [1] and, when Au nanorods were present in the sample, the Ag 2p core level [1] of the substrates on which the graphitic material was deposited. Spectral analysis included a Shirley background subtraction [1] and peak separation using mixed Gaussian-Lorentzian functions in a least squares curve-fitting program (Winspec) developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. The substrates were evaporated gold films supported on mica (cleaned in an ozone discharge for 15 min, followed by sonication in ethanol for

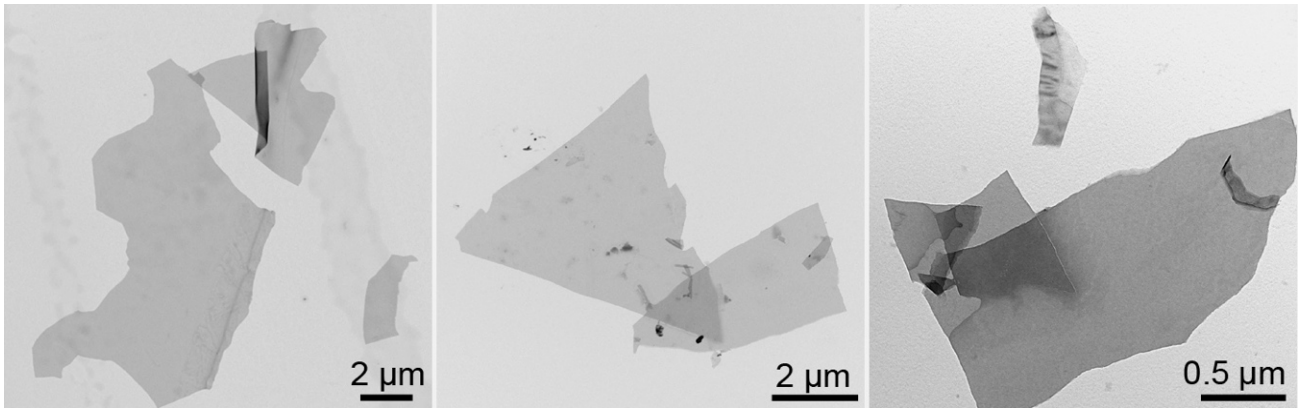
20 min immediately before being employed) or, when the sample contained Au nanorods, Ag foil (purity 99.99%, Goodfellow, U.K.) which was polished (Brasso metal polish, Reckitt Benckiser UK Ltd., U.K.) to remove most of the impurities from the surface, sonicated in ethanol for 20 min and dried in an oven (Thermo Electron Corporation, U.S.A.) at 65°C immediately before being employed. The samples were dispersed by sonication, then a drop was cast on the substrate and left to dry. Raman spectra were recorded with an Invia Renishaw microspectrometer equipped with a He-Ne laser at 633nm using the 100 X objective. Samples were prepared by drop casting of the dispersion on silicon oxide surfaces (Si-Mat silicon wafers, CZ) and the solvent was let to evaporate. For Raman analyses 30 spectra were taken of each sample.



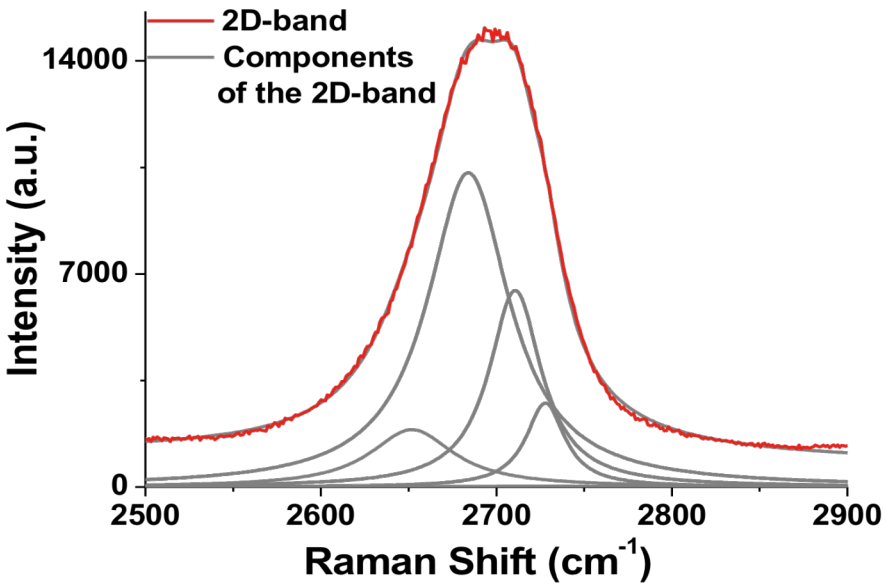
SI-1. Starting and control materials. TEM micrographs of solution cast of **G-1**(a) and **G-DMF** (b). c) Comparison of Raman spectra at 633 nm for **G-1** and **G-DMF**. d) Comparison of the C 1s XPS analysis of **G-1** and **G-DMF**.



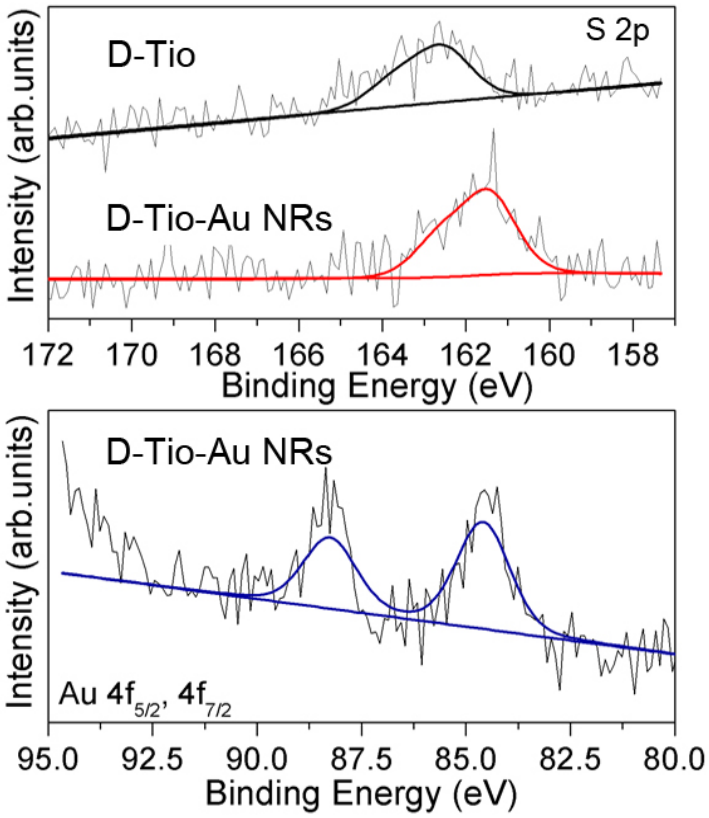
SI-2. TEM micrographs of a. Au NRs dispersed in DMF, b. **CNF-Tio**, c. **CNF-Tio-**Au NRs; d. UV spectra of Au NRs (shown in a) and **CNF-Tio-**Au NRs (shown in c).



SI-3. TEM micrographs of **G-Tio sheets.**

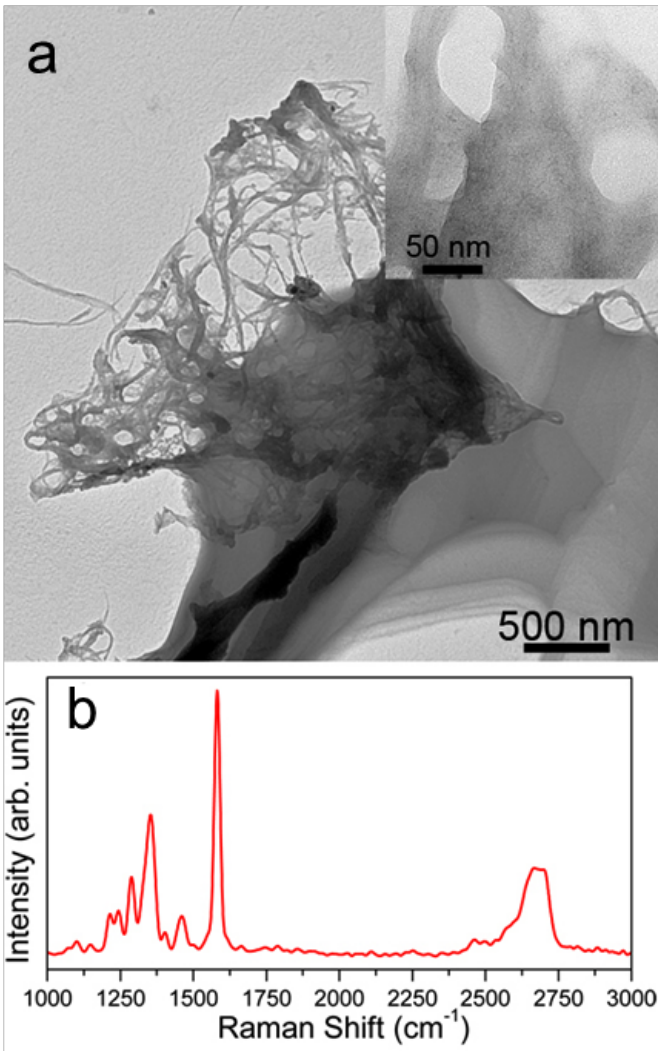


SI.4. Raman analysis of the 2 D band of **G-Tio**. The fitting of the curve identifies deposited graphene as 87 % of bilayer (from 30 spectra).[1]



SI-5. S 2p, Au f XPS of **D-Tio** and after mixing with Au NRs.

The fact that cavitation energy plays a key role in the exfoliation and the formation of nanofibers processes can be verified by increasing the temperature of the system to room temperature (25 °C). When G-Tio dispersions are ultrasonicated at higher temperature, the chemical attack can be clearly observed by the complete destruction of the graphene sheets close to the edges. The Raman spectra of the products shown testify to the damage of the material.



SI-6. a) TEM micrograph of **D-Tio** prepared at 25 °C and b) Raman spectra of the sample showing a large damage in the graphene structure.

[1] A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S, Roth, A. K. Geim, *Phys. Rev. Lett.* 2006, **97**, 187401-1.